Orbital ordering in manganites in the band approach.

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We consider the orbital ordering in LaMnO$_3$ and similar systems, proceeding from the band picture. We show that for the realistic magnetic structure of A-type there exists a complete nesting betweeen two e_g-bands. As a result there occurs an instability towards an excitonic insulator-like state – an electron-hole pairing with the wave vector $Q = (\pi, \pi)$, which opens a gap in the spectrum and makes the system insulating. In the resulting state there appeasr an orbital ordering – orbital density wave (ODW), the type of which coincides with those existing in LaMnO$_3$.

INTRODUCTION

Manganite oxides R$_{1-x}$M$_x$MnO$_3$ (R=La, Pr, Nd,... and M = Ca, Sr) attract great interest both from experimental and theoretical points of view. The phase diagram of these compounds is very rich, and in large part of it there exist, besides magnetic, also an orbital ordering due to the Jahn-Teller nature of Mn^{+3} ions with configuration $t_{2g}^3 e_g$. Usually this ordering, especially at the end of the series RMnO$_3$ (x=0) is described in the picture of localized d-electrons [1]. However it was recently shown [2, 3, 4] that the orbital structure of doped materials can be rather successfully explained from the opposite, band structure point of view – at least for the e_g-electrons. Experimentally manganites are not very far from the metallic state. Although being insulating, undoped LaMnO$_3$ has relatively small energy gap, by optical data of the order of 0.4 eV [5]. Moreover the conductivity of RMnO$_3$ considerably increases above the temperature of the orbital ordering [7]. Thus the question whether one can explain the main properties of undoped RMnO$_3$ materials, in particular their insulating character and the orbital ordering, proceeding from the band structure point of view, has a great interest.

The first attempt in this direction was undertaken by Gor'kov and Kresin [8] who wrote down the spectrum of e_g - electrons on a cubic lattice in a general form based only on symmetry arguments. However they did not take into account particular relations between hopping matrix elements for the e_g-electrons, and did not discuss the specific features of the Fermi-surface, such as nesting, which play crucial role in our treatment

In the present paper, following the works [2, 4, 8], we consider the ground state of LaMnO$_3$ from the band structure point of view. We show that in the framework of the double-exchange picture there exist perfect nesting between the "electron" and "hole" pockets of two e_g-bands for the realistic magnetic structure of A-type (ferromagnetic planes stacked antiferromagnetically), and also for the hypothetical ferromagnetic state. As a result

of the nesting the system is unstable against electron-hole pairing of the excitonic insulator type. Correspondingly the quasiparticle spectrum develops an energy gap, and the system becomes insulating. The pairing occurs with the wavevector $Q = (\pi, \pi)$ forming two sublattices which correspond to orbital ordering. The type of this orbital ordering obtained theoretically coincides with that observed in LaMnO$_3$ experimentally, although the magnitude of it and of corresponding lattice distortions in this weak coupling scheme is smaller than that existing in reality. Thus we show that the type of the ground state, its insulating character and the symmetry of orbital ordering is reproduced correctly not only from the localized, but also from the itinerant point of view.

We do not claim, of course, that the real LaMnO$_3$ is fully described by the weak coupling approach: in real systems the electron correlations are definitely substantial. Nevertheless, the actual material may show the features typical for both the limiting situations, and therefore we believe that the treatment carried out in this paper, which proceeds from the band picture, may be quite useful and instructive.

THE MODEL

In our calculations we use the tight binding approach for the band structure of manganites, where both double exchange and superexchange are incorporated. In the double-exchange framework with the strong on-site Hund's rule coupling the motion of e_g-electrons is largely determined by the underlying magnetic structure. In this scheme the stability of various magnetic and orbital structures is determined by the competition of the band energy of the e_g-electrons, favoring ferromagnetism, and superexchange interaction J between localized (t_{2g}) spins, favoring antiferromagnetism.

The effective hopping matrix elements $t_{ij}^{\alpha\beta}$ depend on the type of the orbitals α, β and relative orientation of a pair i, j, so that $t_{i,j\|x}^{x^2-y^2, x^2-y^2} = 3/4t$, $t_{i,j\|z}^{z^2, z^2} = t$,

$t_{ij\|x}^{z^2,z^2} = 1/4t$, etc [6]. Besides this, there is the usual dependence of the hopping on the angle θ between neighboring spins: $\tilde{t}_{i,j}^{\alpha,\beta} = t_{ij}^{\alpha,\beta} \cos\theta_{ij}/2$. The antiferromagnetic superexchange energy per bond is $J\cos\theta_{ij}$.

Thus for this model with the infinite Hund energy we come to the double exchange Hamiltonian:

$$H = -\sum \tilde{t}_{ij}^{\alpha\beta} c_{\alpha;\sigma i}^\dagger c_{\beta;\sigma j} + J\sum \mathbf{S}_i \mathbf{S}_j, \qquad (1)$$

to which we will add later the electron-electron interaction. The localized (t_{2g}) spins are treated classically. The last term in the Hamiltonian is repulsive electron-electron on-site interaction.

Using

$$a_1^\dagger = \sum_i e^{i\mathbf{p}\mathbf{R}_i}(\alpha_{\mathbf{p}} c_{|x^2-y^2\rangle i}^\dagger + \beta_{\mathbf{p}} c_{|z^2\rangle i}^\dagger) \qquad (2)$$

$$a_2^\dagger = \sum_i e^{i\mathbf{p}\mathbf{R}_i}(-\beta_{\mathbf{p}} c_{|x^2-y^2\rangle i}^\dagger + \alpha_{\mathbf{p}} c_{|z^2\rangle i}^\dagger) \qquad (3)$$

it is straightforward to calculate the band dispersion and total energy of different phases (cf. [2, 4]). For example for the simplest case of A-type antiferromagnetic ordering one has the following bands:

$$\varepsilon_{1,2}(\mathbf{p})/t = -\Big[\cos p_x + \cos p_y \qquad (4)$$
$$\pm \left(\cos^2 p_x + \cos^2 p_y - \cos p_x \cos p_y\right)^{1/2}\Big],$$

and for the ferromagnetic case one has

$$\varepsilon_{1,2}(\mathbf{p})/t = -\Big[\cos p_x + \cos p_y + \cos p_z \qquad (5)$$
$$\pm \big(\cos^2 p_x + \cos^2 p_y + \cos^2 p_y - \cos p_x \cos p_y$$
$$- \cos p_x \cos p_z - \cos p_y \cos p_z\big)^{1/2}\Big]$$

It is instructive to look at the form of the Fermi-surface for different concentration of electrons. For the A-type magnetic structure with increasing number of electrons n in e_g-bands ($n = 1 - x$ in La$_{1-x}$Ca$_x$MnO$_3$) we first start to fill the band ε_1 in (4). It has predominantly $|x^2 - y^2\rangle$-character close to the Γ-point (center of the Brillouin zone). The second band ε_2 begins to fill from $n \approx 0.14$, creating the second pocket of the Fermi-surface. The evolution of the Fermi-surface is shown schematically in Fig. 1

We see that by approaching $n = 1$ (the case of the undoped LaMnO$_3$) the shape of the Fermi-surface pockets becomes more and more "flat". Although for $n = 1$ one can not speak about electrons and holes in strict sense, from the sequence of the filling (Figs. 1 a-d) it is clear that one should treat the inner pockets of the Fermi-surface as electron, and the outer one - as hole-like. It is true at least for n slightly less than one.
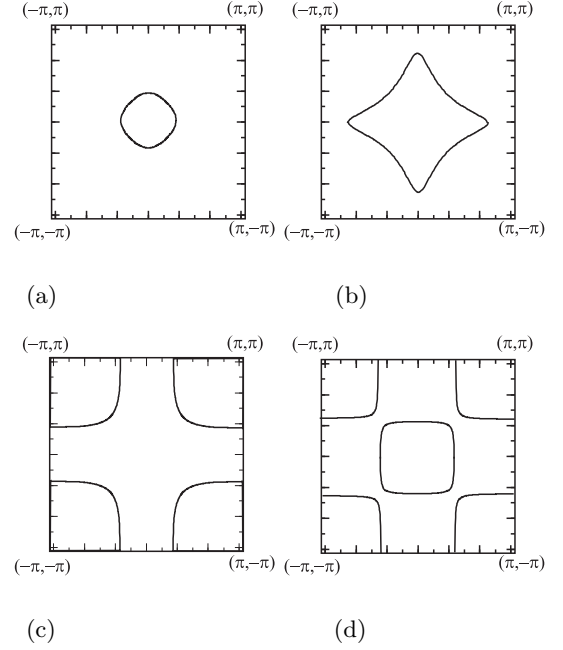

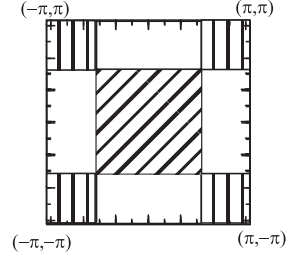FIG. 1: Evolution of the Fermi-surface with increasing the electron concentration n

FIG. 2: Fermi surface in the limit $n \to 1$. The "electron" pocket is shown by the diagonal hatching; "hole" – by vertical

It is also clear that for $n = 1$ there exist perfect nesting between the bands 1 and 2: their Fermi-surfaces coincide with the shifting by the wavevector $Q = (\pi, \pi)$. It can be seen directly from the Eq. 4. For $n = 1$ one has

$$\varepsilon_1(\mathbf{p} + \mathbf{Q}) = -\varepsilon_2(\mathbf{p}) \qquad (6)$$

The spectrum (5) for the ferromagnetic phase (3D - case) obeys the same relation (6) with the wave vector $Q = (\pi, \pi, \pi)$. Hence the full nesting between the bands 1 and 2 take place also in the ferromagnetic case, although the Fermi surface is not flat anymore.

EXCITONIC INSTABILITY AND PAIRING

It is well known, that in the situation of nesting the original homogenous metallic state of the system is unstable. Depending on the dominant interactions different

types of ordering state may exist: those with singlet or triplet, real or imaginary order parameters, etc. [12]

In order to study the consequences of nesting for magnetically ordered materials we assume the magnetic order of localized spins of A-type. We want to note that due to the large Hund's coupling there is no hopping from one ferromagnetic plane to another and the spin indexes are fixed. But instead of the spin degeneracy, which is lifted, we have here another degree of freedom - double orbital degeneracy, which plays the role of spins in the nondegenerate case. Thus for the repulsive electron-electron interaction, which we assume, we would have, instead of the formation of a spin density wave (SDW) state, the corresponding formation of its orbital analog - orbital density wave (ODW). We will show that this state is indeed realized in our case. The new ground state in case of nesting can be easily found in the standard Green function technique (cf. for example [10, 11]). We will consider the case of the A-phase. The ferromagnetic case may be studied along the same lines.

Due to coupling between the two bands (4) the anomalous Green function arises. It is obvious that while normal Green functions $G^{11}(\mathbf{p})$ and $G^{22}(\mathbf{p})$ are proportional to $\delta_{p,p'}$, the anomalous Green function $G^{12}(\mathbf{p},\mathbf{p}')$ is proportional to $\delta_{p+Q,p'}$. Further we will use notation $G^{12}(\mathbf{p})$ for the sake of simplicity. In general the equations for the Green functions can be written in the following form:

$$(i\omega_n - \varepsilon_2(\mathbf{p}) + \mu)G^{22}(\mathbf{p},\omega_n) = 1 + \Sigma^{12}(\mathbf{p},\omega_n)G^{12}(\mathbf{p},\omega_n)$$

$$(i\omega_n - \varepsilon_1(\mathbf{p}) + \mu)G^{12}(\mathbf{p},\omega_n) = \Sigma^{12}(\mathbf{p},\omega_n)G^{22}(\mathbf{p},\omega_n)$$

where

$$\Sigma^{12}(\mathbf{p},\omega_n) = \qquad (7)$$
$$-T\sum_m \int \frac{d\mathbf{p}}{(2\pi)^3}\Gamma^{12}(\mathbf{p},\mathbf{p}',\omega_n-\omega_m)G^{12}(\mathbf{p},\omega_m)$$

with $\Gamma^{12}(\mathbf{p},\mathbf{p}',\omega_n-\omega_m)$ being the repulsive electron-electron interaction. Using $\varepsilon_1(\mathbf{p}) = -\varepsilon_2(\mathbf{p}+\mathbf{Q}) = \varepsilon(\mathbf{p})$ one can write:

$$G^{22}(\mathbf{p},\omega_n) = -\frac{i\omega_n + \varepsilon(\mathbf{p})}{\omega_n^2 + \varepsilon^2(\mathbf{p}) + |\Sigma^{12}(\mathbf{p},\omega_n)|^2} \qquad (8)$$

$$G^{12}(\mathbf{p},\omega_n) = -\frac{\Sigma^{12}(\mathbf{p},\omega_n)}{\omega_n^2 + \varepsilon^2(\mathbf{p}) + |\Sigma^{12}(\mathbf{p},\omega_n)|^2} \qquad (9)$$

$$\Sigma^{12}(\mathbf{p},\omega_n) = -T\sum \int \frac{d\mathbf{p}'}{(2\pi)^3}\Gamma^{12}(\mathbf{p},\mathbf{p}',\omega_n-\omega_m)$$
$$\times \frac{\Sigma^{12}(\mathbf{p},\omega_m)}{\omega_m^2 + \varepsilon^2(\mathbf{p}) + |\Sigma^{12}(\mathbf{p},\omega_m)|^2} \qquad (10)$$

Assuming $\Gamma^{12}(\mathbf{p},\mathbf{p}',\omega_n-\omega_m)$ being independent on frequency one gets that $\Sigma^{12}(\mathbf{p},\mathbf{p}',\omega_n,\omega_m)$ is also frequency-independent. The quantity

$$E = \pm\sqrt{\varepsilon(\mathbf{p})^2 + \Delta^2(\mathbf{p})} \qquad (11)$$

gives the spectrum of elementary excitations with the gap $|\Delta(\mathbf{p})| = |\Sigma^{(12)}(\mathbf{p})|$. The gap can be determined from the following equation

$$\Delta(\mathbf{p}) = \int \frac{d\mathbf{p}'}{(2\pi)^2}\Gamma^{12}(\mathbf{p},\mathbf{p}')\frac{\Delta(\mathbf{p}')}{2E(\mathbf{p}')}\tanh\frac{E(\mathbf{p})}{2T}, \qquad (12)$$

which in the presence of the nesting always has nontrivial solution. For the simple on-site interaction (Hubbard repulsion $Un_{i\alpha\uparrow}n_{i\beta\uparrow}$ with $\alpha \neq \beta$) one gets in the weak-coupling case $U \ll W$ the usual solution with $\Delta(T=0) \sim \varepsilon_F \exp(-W/U)$ with W being bandwidth. One can also show that the results do not crucially depend on the choice of Hubbard interaction, and that they remain qualitatively the same for the electron-electron repulsion of the screened Coulomb type with the screening length larger than the intersite distance.

As we see from Eq.(11), the resulting spectrum has a gap and consequently this state is insulating, in agreement with the insulating nature of LaMnO$_3$. It is also clear that the pairing with the wave vector $Q = (\pi,\pi)$ leads to the formation of the checkerboard-type superstructure in the xy-plane.

Using the inverse transformation of (3) one can find the alternation of the occupation numbers of different orbital states due to interband excitonic pairing (appearance of the anomalous average $\delta n^{(i)}_{|x^2-y^2\rangle|z^2\rangle} = \langle c^\dagger_{|x^2-y^2\rangle i}c_{|z^2\rangle i}\rangle$) as:

$$\delta n^{(i)}_{|x^2-y^2\rangle} = \delta n^{(i)}_{|z^2\rangle} = 0 \qquad (13)$$
$$\delta n^{(i)}_{|x^2-y^2\rangle|z^2\rangle} = (-)^i D, \qquad (14)$$

where $D = G^{12}(x,x)$ and proportional to the energy gap.

The obtained excitonic insulator state corresponds to the formation of an orbitally-ordered state in which in each plane there appears two orbital sublattices of the orbitals $|\phi\rangle = \cos(\phi/2)|z^2\rangle \pm \sin(\phi/2)|x^2-y^2\rangle$ with the angle

$$\tan\phi/2 = \qquad (15)$$
$$\frac{(n_{|z^2\rangle} - n_{|x^2-y^2\rangle})) - \sqrt{(n_{|z^2\rangle} - n_{|x^2-y^2\rangle})^2 + 4D^2}}{2D},$$

where the diagonal averages n_{z^2} and $n_{x^2-y^2}$ for $n = 1$ are slightly different: $n_{z^2} \approx 0.45$, $n_{x^2-y^2} \approx 0.55$ due to specific form of occupied bands. For equal occupation $n_{z^2} = n_{x^2-y^2} = 0.5$ the ordering would correspond to the angle $\phi = \pi/2$, i.e. to the equal mixture of the basis orbitals ($|\pi/2 >= 1/\sqrt{2}(|z^2\rangle \pm |x^2-y^2\rangle)$).

Experimentally it was found that the corresponding orbitals in LaMnO$_3$ are $|\phi \sim \pm 100°\rangle$; this solution in our analysis would be obtained for intermediate Hubbard interaction $W/U \sim 3$. We would like also to note that in the standard treatment of orbital ordering in the picture of localized electrons one obtains close to T_c similar $|\pm\pi/2\rangle$ orbital sublattices [14].

Turning to the ordering in the third direction, for the real A-type magnetic structure we see that in the accepted approximation (no hopping and no dispersion in z-direction) the system "does not know" how to order. If we include certain weak hopping in the z-direction which could appear at finite temperatures and, even at $T = 0$, due to quantum corrections to the leading terms considered here [16], these hopping would lead to the appearance of the main instability at the wavevector $Q = (\pi, \pi, \pi)$, i.e. it would give orbital alternation also in the z-directions. The same type of ordering appears also in the ferromagnetic case. Apparently the experimentally observed ordering, which in $LaMnO_3$ is that with the "in phase" orbital ordering in the z-direction, $Q = (\pi, \pi, 0)$, is caused by some other factors, e.g. an interplay of $GdFeO_3$ distortion (tilting of MnO_6-octahedra) and Jahn-Teller deformations [17].

Referring to the theoretical situation, we should note that in contrast to the usually considered excitonic insulators, for the A-type magnetic structure there exist not only an interband nesting, but for n=1 also each pockets has nesting within itself, with its own vectors $Q_{x,y} = (\pi, 0), (0, \pi)$ (this was also noticed by Hotta [9], who, however, did not consider the interband instability). In principle these two instabilities may coexist and influence one another.

One can show that the inclusion of both these factors just strengthens the excitonic instability and increases the resulting energy gap, without changing qualitative features of the solution. Besides, keeping in mind the sequence of band fillings shown in Figs.1 a-d, we expect that in the realistic situation the interband pairing would dominate and the results presented above would be valid. Besides, intraband nesting exist for $n = 1$ for the A-type structure, but it is absent for the ferromagnetic case.

CONCLUSIONS

Thus we see that one can explain, at least qualitatively, the appearance of an orbital ordering and opening of the gap in the electron energy spectrum of undoped $LaMnO_3$ and similar systems proceeding from the band picture. In this approach orbital ordering appears due to an excitonic instability, caused by the nesting between pocket of two e_g-bands. The resulting state has a correct type and symmetry of the orbital ordering. Thus one can interprets the ground state of $LaMnO_3$ as arising due to this excitonic instability.

Of course, as already mentioned in the introduction, we do not claim that our treatment gives the only correct picture of $LaMnO_3$; there are many indications that the electron correlations in it are relatively strong, so that it is usually rightly treated as a Mott insulator. However the truth is often "in between", the system may show the features of the both the limiting pictures. In any case it is gratifying that one can obtain a quite reasonable description of this system proceeding from the band point of view. This result, in certain sense, completes similar investigations carried out in [2, 3, 4]. In these papers it was shown that the band approach works quite well for description of orbital structure of overdoped, half-doped and less-than-half-doped manganites. It is even somewhat surprising that using the same simple approach one can explain even the properties of an undoped $LaMnO_3$, which until now was always considered as a bona fide Mott insulator. One may hope that this novel point of view may prove useful both for better understanding of the theoretical situation and for the interpretation of certain experiments.

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